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(19) (CA) **APPLICATION FOR CANADIAN PATENT** (12)

(54) Platelet-Like, Surface-Modified Substrates

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Claims

1. Platelet-like, surface-modified substrates obtainable by treating platelet-like substrates using at least difunctional organic coupling agents and then coupling a low molecular weight organic radical to a second functional group of the agent which has been coupled to the substrate.

2. Substrates according to Claim 1, characterized in that the low molecular weight organic radical contains a chromophore group or forms a chromophore group by coupling.

3. Substrates according to Claim 1, characterized in that the low molecular weight organic radical contains a free-radical initiator group or forms a free-radical initiator group by coupling.

4. Platelet-like, surface-modified substrates, obtainable by treating platelet-like substrates with organo-Ti, organo-Zr or organo-Zr/organo-Al coupling agents, characterized in that after the coupling reaction to the coupled agent, a second functional group is available for coupling to a low molecular weight organic radical.

5. Process for the preparation of substrates according to Claim 1, characterized in that platelet-like substrates are reacted in an aqueous or an organic medium or in a mixture thereof with the coupling agent and then the low molecular weight organic radical is coupled, or that initially a coupling agent containing the low molecular weight organic radical is prepared and is then reacted with the substrate.


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Platelet-like, surface-modified substrates

The invention relates to platelet-like, surface-modified substrates, obtainable by treating platelet-like substrates using at least di-functional organic coupling agents and then coupling a low molecular weight organic radical to a second functional group of the agent which has been coupled to the substrate.

Platelet-like substrates, i.e. materials having a relatively small thickness in relation to length and width are used in many fields of technology. For instance, platelet-like minerals such as, for example, kaolin, mica or talc are used in finely divided form as fillers for plastics. Platelet-like pigments such as, for example, metal oxide-coated mica platelets or platelet-like iron oxide or bismuth oxychloride are used not only in the pigmenting of, for example, paints, colorants, plastics and the like but also in cosmetic preparations.

The ever increasing utility of platelet-like substrates in different industrial fields increasingly requires the development of surface-modified substrates ultimately to ensure the compatibility of the substrates with further components present in industrial compositions.

A fundamental problem is the strong tendency of platelet-like substrates of this type to form agglomerates in which the substrates are present lying on top of one another like a deck of cards and can only be separated again with difficulty owing to strong adhesion. This is all the more troublesome since, on incorporating platelet-like substrates in formulations, high shear forces cannot be applied owing to the fragility of the thin substrates.

Numerous methods have therefore been developed, inter alia, to solve the problem of incorporating platelet-like pigments, in particular, into thermoplastic materials (DE-A-2,603,211, DE-A-3,221,044, DE-A-3,627,329).

Furthermore, coatings employing polysiloxanes for improved weathering resistance have been disclosed (DE 3,334,598), and also treatment with coupling agents such as organotitanates to give improved dispersibility in cosmetic preparations (EP 0,306,056), and with organosilanes to give improved water resistance (EP 0,268,918).

The object of the present invention is to develop other and better processes for surface modification of platelet-like substrates. In particular, the substrates must be compatible with a great many different industrial formulations without the typical properties of platelet-like substrates being lost. There is a need, inter alia, for platelet-like, surface-modified pigments which can be incorporated in formulations without losing their pigment properties. Examples of frequently encountered disadvantages from pigment incorporation are pigment shock, ie. the formation of agglomerates on incorporation owing to incompatibilities, and pigment migration.

This object is achieved by the present invention. In particular, it has been found that the treatment of platelet-like substrates with organic coupling agents which have at least one other functional group for coupling to a low molecular weight organic radical allows the preparation of surface-modified substrates having virtually any desired functional properties, depending on the type of low molecular weight organic radical.

The present invention accordingly provides platelet-like surface-modified substrates, obtainable by treating platelet-like substrates with at least di-functional organic coupling agents and then coupling a low molecular

weight organic radical to a second functional group of the agent which has been coupled to the substrate.

The invention also provides platelet-like surface-modified substrates, obtainable by treating platelet-like substrates with organo-Ti, organo-Zr or organo-Zr/organo-Al coupling agents, characterized in that after the coupling reaction to the coupled agent, a second functional group is available for coupling to a low molecular weight organic radical.

Furthermore, the present invention provides a process for the preparation of substrates according to Claim 1, characterized in that platelet-like substrates are reacted in an aqueous or an organic medium or in a mixture thereof with the coupling agent and then the low molecular weight organic radical is coupled, or in that initially a coupling agent containing the low molecular weight organic radical is prepared and is then reacted with the substrate.

Finally, the invention provides the use of the surface-modified substrates according to Claim 1 in formulations such as paints, dye compositions, plastics and cosmetics. The invention ultimately provides formulations which contain the substrates according to the invention.

Preferred platelet-like substrates for surface modification according to the invention are, in particular, layer-structured silicates and oxides or oxide-coated materials, since these have reactive OH groups on their surface. Examples of these are, on the one hand, mica, talc, kaolin or other comparable minerals and, on the other hand, also platelet-like iron oxide, bismuth oxychloride and the metal oxide-coated micas known as pearl lustre pigments, and also aluminium platelets or metal oxide-coated metal platelets, in particular metal oxide-coated aluminium platelets. All conventional pearl lustre pigments can be used, for example mica coatings

containing coloured or colourless metal oxides such as TiO_2, Fe_2O_3, SnO_2, Cr_2O_3, ZnO and other metal oxides as such or mixed in a uniform layer or in successive layers. These pigments have been disclosed, for example, in the German Patents and Patent Applications 1,467,468, 1,959,998, 2,009,566, 2,214,545, 2,215,191, 2,244,298, 2,313,331, 2,522,572, 3,137,808, 3,137,809, 3,151,343, 3,151,354, 3,151,355, 3,211,602 and 3,235,017.

The surface-modified substrates according to the invention are prepared by reacting the substrates, for example with at least di-functional organic coupling agents. Then a remaining functional group of the coupled agent is reacted with a low molecular weight organic radical. However, it is also possible first to prepare the coupling agents which have been linked to the low molecular weight organic radical and then to react these coupling agents with the platelet-like substrate. Depending on the structure of this radical, this gives platelet-like, surface-modified substrates having various properties.

Suitable compounds for use as coupling agents which have not themselves yet been further modified are described, for example, in the following publications:

Edwin P. Plueddemann; Silane Coupling Agents; Plenum Press; New York, London (1982) and the literature referred to therein. Salvatore J. Monte, Gerald Sugerman; Ken-React Reference Manual - Titanate, Zirconate and Aluminate Coupling Agents (1987) and the literature referred to therein. Dynasilan Haftvermittler, Organofunktionelle Silane, Technische Information Dynamit Nobel (1985). Lawrence B. Cohen, The Chemistry of Zirconaluminate Coupling Agents and their Application in High Solids Coatings, Water-borne and Higher-Solids Coatings Symposium, New Orleans, 1986. Lawrence B. Cohen, Corrosion Reduction in High Solids and Water-borne Coatings using Zirconaluminate Adhesion Promoters, Water-

borne and Higher-Solids Coatings Symposium, New Orleans, 1988. Peter Z. Moles, The Application of Zirconium Compounds in Surface Coatings, Water-borne and Higher-Solids Coatings Symposium, New Orleans, 1987.

As a rule, suitable compounds contain one or more metal centres such as Si, Ti, Zr or Al to which functional organic groups are bonded. Examples of suitable silanes are the commercially available polyfunctionalized DYNASYLAN® agents (Dynamit Nobel). These are alkoxysilane derivatives having two or three alkoxy radicals and one or two alkyl radicals to which functional groups have additionally been bonded, for example amino, mercapto or a nitrile group or a halogen radical such as chlorine. Examples of suitable titanate coupling agents are the commercially available "KR" materials (Kenrich Petrochemicals, Inc.). Like the abovementioned silanes, these agents are compounds having alkoxy radicals and radicals additionally substituted by functional groups, the radicals of the said compounds being bonded via oxygen to the metal centre. Examples of the functional groups are amino, mercapto or hydroxyl groups.

Examples of suitable zirconate coupling agents are the neoalkoxy zirconates having amino or mercapto groups obtainable from Kenrich Petrochemicals, Inc. under the designation "LZ" agents. Furthermore, the substrates according to the invention can be prepared using zirconium aluminates such as, for example, the appropriate "Cavco Mod" agents obtainable from Cavedon Chemical Co., Inc. Platelet-like metal substrates, for example platelets of Al, Cu, Zn or alloys thereof, are also suitable for coatings using zirconium aluminates.

The coupling agents are applied either directly or by intensive mixing of substrate and coupling agent, preferably, however, in organic solvents or in aqueous medium. The concentration of the coupling agent in these procedures is in the range from about 0.01 to 20,

preferably 0.1 to 10% by weight, relative to the substrate.

Then a still intact functional group of the agent which has been applied to the substrate is coupled to a low molecular weight organic radical. It is possible, for example, to react a chromophore-containing radical with the modified substrate. By virtue of the high degree of variation, excess is thus available to virtually colours which, as surface colours, by interaction with the surface colours of the substrates themselves and in particular with the interference colours of the pearl lustre pigments give any desired colour effect.

Primary aromatic amines are particularly suitable functional groups for coupling a chromophore-conferring organic radical. The complete colour spectrum from yellow through orange, red, bordeaux, blue to brown and black is accessible by direct azo-coupling using the coupling agents known from azo dye and pigment chemistry (W. Herbst, K. Hunger, Industrielle Organische Pigmente, published by VCH Verlagsgesellschaft mbH, Weinheim (1987) and P. Rys, H. Zollinger, Leitfaden der Farbstoffchemie, published by Verlag Chemie, Weinheim (1976)).

The preparation of the preferred chromophore-containing substrates according to the invention is accordingly carried out by first reacting the substrate with an organic coupling agent containing an aromatic primary amine and, if desired, after isolating the modified substrate, by diazotizing the amine and reacting this functional group with a coupling component by conventional methods.

Examples of suitable coupling agents are:

Isopropyl 4-aminophenylsulphonyl di(dodecylphenylsulphonyl) titanate (KR 26S), 4-aminophenylsulphonyl dodecylphenylsulphonyl ethylene-

titanate (KR 226S), isopropyl tri(2-aminobenzoyl) titanate (KR 52S), isopropyl di(4-aminobenzoyl) isostearoyl titanate (KR 37BS) and neopentyldiallyloxy tri(m-aminophenyl) zirconate (LZ 97). However, it is also possible to use other coupling agents in which one functional group, after reaction with the substrate, is suitably transformed so that a couplable amino group is available. Alternatively, it is also possible to carry out the azo coupling on the coupling agent itself and, as the final process step, to couple the modified coupling agent to the platelet-like substrate. Furthermore, it is possible first to prepare an azo-dye compound and to convert this into a coupling agent.

Moreover, it is possible to couple low molecular weight organic radicals to one functional group of the agent which has been coupled to the substrate, these organic radicals containing a free-radical initiator function or to form a function of this type only after the coupling has taken place. Similarly to the abovementioned azo dyes, it is possible, on the one hand, to form typical azo initiator groups which can be prepared from primary aromatic amines (azo components originating from the coupling agent). On the other hand, aliphatic azo initiator groups are also accessible.

For instance, an initiator such as 4,4'-azo-bis(4-cyanopentanoic acid) (Fluka AG) can be converted into an acid derivative using a functional group of a coupling agent, such as $-NH_2$, -OH or -SH. The corresponding reaction are preferably carried out under mild conditions.

Moreover, it is possible by the process according to the invention to bond photoinitiators via a coupling agent to platelet-like substrates by reacting compounds of the general formula

RG-A-IN

with a functional group of the coupling agent which may

already have been coupled to the substrate. RG is a reactive group such as -OH, -SH, $-NH_2$, -halogen, -COOH or $-CONH_2$; A, a spacer group, normally an alkylene chain which is optionally interrupted by hetero atoms such as -O-, -S-, -NH- or carbonyl, carboxyl, carboxamide groups or similar groups; and IN is a photoinitiator base structure.

Suitable compounds for this purpose whose mode of preparation and reactions of the group RG can give covalent linkage to matrix systems without loss of initiator activity, are described in detail in DE-A-3,738,567 and are similarly wholly applicable to the present invention. This gives access to all well known and currently used photoinitiator structures of the hydroxy- or amino-alkylphenone type, and also to derivatives of benzoin ethers, benzyl ketals, dialcoxyacetophenones, thioxanthones, and acylphosphine oxides for the purposes of surface-modification according to the invention.

In a similar manner to the abovementioned formation of chromophore groups, it is also usually possible in this case first to introduce a free-radical initiator group by covalent bonding to the coupling agent itself. Then the modified coupling agent is reacted with the platelet-like substrate.

Depending on the intended use of the platelet-like, surface-modified substrate which has been prepared according to the invention, other low molecular weight organic radicals can be covalently bonded to one functional group of the coupling agent.

The type of surface-modification according to the invention gives a number of advantages. For instance, it has been observed that the covalent linking of chromophores to the pigment matrix within the scope of the process according to the invention ensures a permanent coating of the pigments with the chromophore.

This is often not the case according to the prior art, particularly with regard to purely physical coating. However, it is even more surprising that in the case of pearl lustre pigments, modification according to the invention allows the properties typical of these pigments to be retained. This is true, in particular, of the pearl lustre effect, which with the substrates according to the invention by interaction with the intrinsic colours of the chromophore, allows virtually any colour effect to be achieved.

The particular combination of permanent coating and a high degree of variability of colour shades and effects is of exceptionally great practical use in numerous formulations such as paints, for example car body finishes, cosmetics, plastics and dye compositions.

Substrates according to the invention in which free-radical initiator groups have been covalently bonded have surprising advantages on incorporation in polymer systems. For instance, polymers having improved pigment dispersion are obtained if a monomer system containing finely dispersed initiator pigment is polymerized. Since the polymerization is initiated at the pigment surface, the degree of dispersion in the polymer is virtually unaltered.

This reaction sequence has particular utility in emulsion polymerizations.

The modified platelet-like substrate is finely dispersed, for example in an aqueous solution containing an emulsifier. The emulsifier molecules then become preferentially attached to the hydrophobic pigment particles so that ultimately the hydrophilic emulsifier molecules are directed into the aqueous phase. This gives micelle-like structures which fill up with monomer. Polymerization then occurs almost without exception in the pigment micelles (C.H.M. Caris et al.,

"Polymerization at the surface of inorganic submicron particles", XIX FATIPEX Kongreß, Aachen 1988). The application of this process principle allows all polymer reactions which are feasible in emulsion, for example the polymerization and copolymerization of styrene, vinyl acetate, butadiene, isoprene, acrylonitrile or vinyl chloride, to be carried out on platelet-like substrates which bear initiator groups. The reaction conditions are known to a person skilled in the are and can be taken, for example, from: D.B. Braun et al. in "Praktikum der makromolekularen organischen Chemie", published by Hüthig-Verlag, Heidelberg 1979.

The polymer-encapsulated pigments which have been prepared in this manner can be significantly better incorporated in polymer systems and also have improved weathering resistance. There is virtually no loss of lustre or formation of agglomerates.

Furthermore, it is not necessary to isolate the polymer-encapsulated substrate particles. The substrate/polymer particles formed as pigment latices in the emulsion polymerization can be mixed directly with the components of a waterborne paint system by latex-intermixing. In this procedure, the polymer coating of the platelet-like substrates can be optimally adapted to the paint system by the appropriate selection of the monomers. The mixing of the harmonized latices allows any incompatibilities and any imperfections in the paint system caused by pigment addition (pigment shock) to be for the greatest part or even completely eliminated.

Example 1

100 g of Iriodin® 103 (titanium dioxide-coated mica flake pigment from E. Merck, Darmstadt) are treated to activate the calcined titanium dioxide surface by coating with approximately 7.3% of freshly precipitated titanium hydroxide oxide in aqueous solution (pH 2.2). This is

achieved by metering an aqueous solution of titanium tetrachloride (350 g/l) into the aqueous suspension of the pigment which has been adjusted to a pH of 2.2 using 10% hydrochloric acid, and keeping the pH value constant meanwhile using 10% sodium hydroxide solution. The pigment is then filtered, washed with water and dried.

100 g of the pre-treated pigment are suspended in 500 ml of toluene. Then a solution of 10 g of KR26S (isopropyl 4-aminophenylsulphonyl di(dodecylphenylsulphonyl) titanate from Kenrich Petrocehmicals, Inc., Bayonne, New Jersey) in 75 ml of toluene is added. After stirring for 2 h at room temperature, the pigment is filtered off, washed with toluene and dried in vacuo.

100 g of the KR26S-modified pigment are suspended in 150 ml of completely deionized water. To the pigment suspension are then added 11.8 ml of 5% hydrochloric acid and the mixture is cooled to -2°C. To the cooled, acidic pigment suspension is then added in the course of 20 min a solution at -5°C of 0.94 g (0.27 mol) of sodium nitrite in 50 ml of deionized water. During this operation, the temperature increases to +2°C. Potassium iodide/starch paper is used to test for nitrite and hence for the completion of the reaction. Excess nitrite is destroyed using urea.

After the diazonium salt formation has ceased, the suspension of the pigment/diazonium salt is slowly run in, with stirring, to a solution at 5°C of 0.98 g (5.5 mmol) of acetoacetanilide in 170 ml of 5% hydrochloric acid. During this operation, the temperature increases to 10°C and a light yellow pigment suspension is obtained. After addition to the acetoacetanilide has ceased, stirring with cooling is maintained for a further 2 h. Then the pigment is filtered off under suction, washed with water and dried.

If the coupling is carried out in alkaline medium at a pH

of about 10, a reddish-orange pigment suspension is obtained.

A similar procedure is used with the following coupling components:

2-Hydroxynaphthalene (β-naphthol)
2-Hydroxy-3-naphthoic acid and also the 2'-hydroxy-3'-naphthoylanilines Naphtol AS®, Naphtol AS-O and Naphtol AS-OL, known as the Naphtol AS® agents (Hoechst AG).

All of the modified platelet-like substrates have high weathering resistance, can be very readily incorporated in industrial formulations with high migration resistance and colour stability without loss of lustre.

Example 2

The procedure of Example 1 is used to modify Iriodin® 103. The organic coupling agent used is LZ97 (neopentyl-diallyloxy tri(m-aminophenyl) zirconate from Kenrich Petrochemicals, Inc.).

To a solution of 10 g of LZ97 in 500 ml of acetone are added in portions 100 g of activated Iriodin® 103. The solid is then filtered off, washed with acetone and dried in vacuo.

In the subsequent diazotization and coupling, the amounts given in Example 1 are trebled in accordance with the stoichiometry of the coupling agent. This gives a reddish brown pigment suspension.

The coupling components given in Example 1 are similarly used.

All of the modified platelet-like substrates have high weathering resistance, can be very readily incorporated in industrial formulations with high migration resistance

and colour stability without loss of lustre.

Example 3

200 g of Iriodin® 504 (iron(III) oxide-coated mica flake pigment from E. Merck, Darmstadt) are suspended in 4 l of deionized water. The suspension is heated to 75°C with vigorous stirring. The pH is adjusted to 6.5 using 15% aqueous sodium hydroxide solution. Then, in the course of 10 min, a solution of 10 mmol of 4-[2-(3-triethoxysilylpropoxy)-ethoxy]-phenyl (2-hydroxy-2-propyl) ketone (preferable in accordance with DE-A-3,738,567) in 200 ml of ethanol is added dropwise to the pigment suspension. During this operation, the pH is kept constant using 5% aqueous sodium hydroxide solution. After the addition has ceased, the mixture is stirred for a further 30 min at 75°C. Then the product is filtered off under suction through a filter funnel, washed with deionized water and dried in vacuo.

Surface-modified substrates are similarly prepared using:

4-[3-(Triethoxysilyl)propoxy]-phenyl (2-hydroxy-2-propyl) ketone

4-[2-(3-Triethoxysilylpropylthio)-ethyl]-phenyl (2-hydroxy-2-propyl) ketone

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Abstract

Plate-like, surface-modified substrates, obtainable by treating platelet-like substrates using at least dysfunctional organic coupling agents and then coupling a low molecular weight organic radical to a second functional group of the agent which has been coupled to the substrate, are eminently suitable for use in formulations such as paints, dye compositions, plastics and cosmetics.